

# PATENT SPECIFICATION

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## (54) PRODUCTION OF ACETYLENE GLYCOLS

(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of 5 Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

10 The invention relates to a process of the production of an acetylene glycol by reaction of an aldehyde or ketone with an acetylene monoalcohol.

15 The production of acetylene glycols by reaction of acetylene monoalcohols with carbonyl compounds in the presence of potassium hydroxide has been described repeatedly (Izv. Akad. SSSR (1967) pages 2107—2109, J. Gen. Chem. USSR, 10, (1940), 480, Chem. Abstr. 34, (1940) 7851, J. Org. Chem. 28 (1963) 2480 and J. Org. Chem. 30 (1965), 3046).

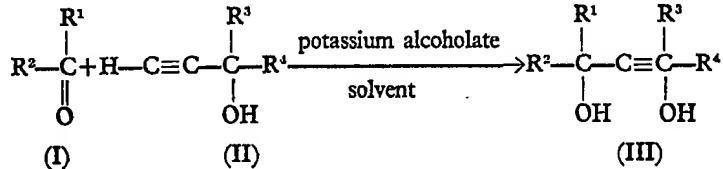
20 The production of bis - tertiary acetylene glycols such as 2,5 - dimethylhexyne - (3) - diol - (2,5), 3,6 - dimethyloctyne - (4) - diol - (3,6) and analogous compounds offers particular difficulty because with potassium hydroxide (which serves as the condensing agent) they form sparingly soluble adducts which, even in solvents such as tetrahydrofuran and dibutyl acetal, cannot be satisfactorily reacted unless a large excess of potassium hydroxide is used.

In contrast to this, the reaction of, for example, propargyl alcohol with acetone or methyl ethyl ketone to form the corresponding acetylene glycol proceeds quite well in tetrahydrofuran when about 1.1 moles of potassium hydroxide powder is used per mole of ketone.

35 Moreover, experiments have shown that acetylene monoalcohols and ketones can be reacted in the presence of potassium hydroxide powder in solvents such as tetrahydrofuran to form the corresponding acetylene glycols in practically quantitative yields. However, from 4 to 5 moles of KOH powder has to be used per mole of acetylene glycol. The reaction also proceeds in solvents such as benzene or toluene, but here again a large excess 40 of potassium hydroxide has to be used.

45 We have now found that the production of an acetylene glycol by reaction of an aldehyde or ketone with an acetylene monoalcohol in a solvent in the presence of a condensing agent having a basic reaction can be carried out with particular advantage by effecting the reaction in an aliphatic hydrocarbon and/or an aromatic hydrocarbon as solvent and by using as the condensing agent a potassium 50 alcoholate of a primary alcohol and/or of a secondary alcohol each of which has four to eight carbon atoms. Such alcohols normally have limited solubility in water.

55 The new process may be represented by the following reaction equation:



70 In this equation, formula (I) denotes the preferred class of aldehydes and ketones. In the case of aldehydes,  $\text{R}^1$  denotes hydrogen and  $\text{R}^2$  denotes hydrogen or an aliphatic, aromatic araliphatic hydrocarbon radical or a

75 heterocyclic radical each having up twenty carbon atoms, preferably hydrogen or an aliphatic or aromatic hydrocarbon radical having up to six carbon atoms. In the case of ketones  $\text{R}^1$  and  $\text{R}^2$  may be identical or different and

- denote aliphatic, araliphatic or aromatic hydrocarbon radicals or heterocyclic radicals each having up to twenty carbon atoms, preferably aliphatic or aromatic hydrocarbon radicals having up to six carbon atoms provided that such radicals are possible in ketones. Alternatively,  $R^1$  and  $R^2$  together with the adjacent carbon atom may form a ring system in which one hetero atom such as nitrogen or oxygen may be included. 5
- Suitable compounds for the production of the acetylene glycols are aliphatic, araliphatic, aromatic and heterocyclic ketones and aldehydes including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2 - ethylhexanal - (1), glycol aldehyde, etherified or esterified glycol aldehydes, benzaldehyde, cinnamic aldehyde, phenylacetalddehyde, furfural, acetone, methyl ethyl ketone, 10 methyl isobutyl ketone, mesityl oxide, acetophenone, benzophenone, piperidone - (4), cyclohexanone, 5 - methylheptan - (6) - one - (2), 6 - methylheptan - (6) - one - (2), geranyl acetone and hexahydrofarnesyl acetone. It is 15 apparent from the foregoing list that the aldehydes and ketones may contain hetero atoms in groupings which do not interfere with the reaction, e.g. ether, carboxylic ester and hydroxy groups as well as heterocyclic rings. 20
- Among these, the following ketones and aldehydes are particularly suitable starting products: propionaldehyde, n - butyraldehyde, isobutyraldehyde, benzaldehyde, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, piperidone - (4), 2 - ethylhexanal - 1,5 - methylhepten - (6) - one - (2), 6 - methylhepten - (6) - one - (2), geranyl acetone and hexahydrofarnesyl acetone. 25
- All primary, secondary and tertiary acetylene monoalcohols having the formula (II) are suitable for the reaction with the carbonyl compounds. The radicals  $R^3$  and  $R^4$  may denote hydrogen atoms and aliphatic, araliphatic and aromatic hydrocarbon radicals and heterocyclic radicals each having up to twenty carbon atoms, but particularly hydrogen and aliphatic or aromatic hydrocarbon radicals having up to six carbon atoms, such as methyl, ethyl, butyl, isobutyl and phenyl. Alternatively,  $R^3$  and  $R^4$  together with the adjacent carbon atom may form a ring system which may contain nitrogen or oxygen as a hetero atom. 30
- Specific examples of acetylene monoalcohols 35 suitable for use in the process according to this invention are: propargyl alcohol, butyn - (1) - ol - (3), 3 - methylbutyn - (1) - ol - (3), 3 - methyl - pentyn - (1) - ol - (3), 3,5 - dimethylhexyn - (1) - ol - (3), 1 - ethynylcyclohexanol - (1), 4 - ethynylpiperidol - (4), phenylethynyl carbinol, 3 - phenyl - 3 - methylpropyn - (1) - ol - (3), hexyn - (1) - ol - (3), 4 - ethyloctyn - (1) - ol - (3), 3,7 - dimethylocten - (7) - yn - (1) - ol - (3), 3,7 - dimethylocten - (6) - yn - (1) - ol - (3) or the 40 dimethyl acetal of 2 - methyl - 2 - hydroxybutyn - (3) - al - (1). It is apparent from the foregoing list that the acetylene monoalcohols may contain heteroatoms in groupings which does not interfere with the reaction, e.g. acetal groups as well as heterocyclic rings. 45
- It is preferred to use 3 - methylbutyn - (1) - ol - (3), 3 - methylpentyn - (1) - ol - (3) and 3,5 - dimethylhexyn - (1) - ol - (3). 50
- Alcoholates which are suitable as condensing agents for the reaction of the aldehyde or ketone with the acetylene monoalcohol are the potassium alcoholates of primary or secondary alcohols having four to eight carbon atoms and particularly the potassium alcoholates of such primary alcohols as n-butanol, isobutanol, n - pentanol, 2 - methylbutanol - (4), 2 - methylbutanol - (1), 2,2 - dimethylpropanol - (1), n - hexanol, 2 - ethylhexanol - (1) and the potassium alcoholates of such secondary alcohols as butanol - (2), pentanol - (2), pentanol - (3), 2 - methylbutanol - (3) and cyclohexanol. The potassium alcoholates of n - butanol and isobutanol are of particular industrial importance. 55
- In the case of these alcohols having only limited solubility in water, the potassium alcoholates can easily be obtained by boiling under reflux an aqueous caustic potash solution, for example a commercial 50% aqueous KOH solution, with excess alcohol and, at the top of a fractionation column, removing the lower aqueous layer from the resulting two-phase azeotrope with water, and returning the alcohol as reflux to the column. In this way a solution of the desired potassium alcoholate is obtained after a short time. After addition of a hydrocarbon which advantageously has a higher boiling point than the alcohol used or which forms with the alcohol an azeotrope whose boiling point is lower than that of the alcohol (for example toluene and isobutyl alcohol, boiling point 101.2°C, with 45% of isobutyl alcohol), the excess alcohol is distilled off. It is also possible, after distilling off of the water/alcohol azeotrope has been completed, to directly remove the alcohol from the solution of potassium alcoholate in excess alcohol by evaporation. To remove the remaining alcohol, the potassium alcoholate formed is heated while stirring at subatmospheric pressure to a temperature of from 100° to 200°C and, after cooling, the powdered potassium alcoholate is stirred with a hydrocarbon to form a suspension. In this way an alcohol-free potassium alcoholate is obtained which is very finely dispersed in the hydrocarbon. The hydrocarbon used is preferably the same as will be used later in the reaction of the aldehyde or ketone with the acetylene alcohol. 60
- Solvents in which the reaction of the aldehyde or ketone with the acetylene monoalcohol using the said condensing agents may be carried out include aliphatic hydrocarbons and aromatic hydrocarbons which are liquid under 65

the reaction conditions and, among these, particularly those having a boiling point range of from 80° to 180°C. Preferred solvents are such aliphatic hydrocarbons as petroleum ether, gasoline mixtures or cycloaliphatic hydrocarbons, e.g. cyclohexane, and such aromatic hydrocarbons as benzene, toluene, xylene, cumene and *p* - diisopropylbenzene or mixtures of these solvents. There is no need to use expensive solvents such as tetrahydrofuran, ether and dioxan.

In carrying out the reaction, the substances participating in the reaction may be added in any sequence. In some cases, particularly in the reaction of acetylene monoalcohols with ketones, it is advantageous to place the suspension of a potassium alcoholate in an aliphatic and/or aromatic hydrocarbon in a vessel and to add the acetylene monoalcohol and the aldehyde or particularly, the ketone while stirring well.

The two reactants are advantageously used in stoichiometric amounts for economic reasons but deviations of up to a few percent are not disadvantageous. The condensing agent is generally used in an amount of from 0.8 to 1.5 moles, preferably from 1 to 1.2 moles, per mole of acetylene monoalcohol. Compounds which are sensitive to atmospheric oxygen are advantageously reacted under an atmosphere of inert gas, e.g. under nitrogen. The solvent is used in such an amount that the reaction mixture can be stirred easily.

The reaction temperature may be chosen within a wide range. In general, temperatures within the range of -20°C to +100°C are suitable, the range of from 0° to +50°C being preferred.

Since the reaction of lower aliphatic ketones with acetylene monoalcohols often results in products which are difficult to stir, it may be advantageous first to carry out the mixing of the reactants at low temperatures, for example from 0° to +10°C, and only then to raise the reaction temperature, for example to 30° to 50°C.

Desirably, the reaction mixture is kept at this temperature for example for one hour to two hours and then such an amount of water is added that all constituents just go into solution and two clear layers are obtained. The lower, aqueous, alkaline layer is separated and the upper, organic layer is neutralized by adding a small amount of an organic or inorganic acid such as formic acid, acetic acid, carbonic acid or sulfuric acid and washed again with water. After the excess solvent has been distilled off, the acetylene glycol formed is obtained in pure condition by distillation *in vacuo*.

Both symmetrical and unsymmetrical acetylene glycols are obtained in the said reaction. They may be used as valuable intermediates; for example the dimethylhexynediol obtained according to Example 1 is a starting material

for the production of chrysanthemum monocarboxylic acid (the parent compound of the insecticides of the pyrethrum group which are nontoxic for warm-blooded animals). Other acetylene glycols may be used for processing into perfumes similar to terpenes or for the production of low lather surfactants. Reaction of the acetylene glycols with hydrogen peroxide results in hydroperoxides which may be used for example as polymerization initiators.

The invention is illustrated by the following Examples, in which parts are by weight.

#### EXAMPLE 1

680 parts of a 50% aqueous caustic potash solution and 3000 parts of isobutanol are boiled while stirring in a flask connected to a distillation column.

475 parts of an aqueous layer is separated in three to four hours from the azeotropic mixture obtained at the top of the column. Then the major portion of the excess isobutanol is distilled off, 1500 parts of xylene are added and the mixture is fractionated while maintaining a good reflux until no more isobutanol leaves at the top of the column (boiling point 136°C).

The potassium isobutyrate suspension is cooled to 0°C and a mixture of 348 parts of acetone and 420 parts of 3 - methylbutyn - (1) - ol - (3) is added in the course of a few minutes with good stirring. The mixture is heated to 30°C and then 750 parts of water are added. Separation into two phases takes place. The lower, aqueous layer is separated. It contains practically no dimethylhexynediol. The upper, organic layer is adjusted to pH 5 with formic acid. After the solvent has been distilled off at about 100 mm Hg, 633 parts of 2,5 - dimethylhexyne - (3) - diol - (2,5) are obtained having a boiling point, at 22 mm Hg, of 121° to 124°C. The yield is 89.5% based on methylbutyn reacted.

#### EXAMPLE 2

A mixture of 420 parts of 3 - methylbutyn - (1) - ol - (3) and 432 parts of methyl ethyl ketone is introduced with good stirring at 0°C into a potassium isobutyrate suspension (prepared as described in Example 1).

The mixture is heated to 30°C and then 650 parts of water is added.

After the xylene has been distilled off from the organic layer, 689 parts of 2,5 - dimethylheptyne - (3) - diol - (2,5) is obtained (boiling point 126° to 133°C at 23 mm Hg); it contains small amounts of 2,5 - dimethylhexyne - (3) - diol - (2,5) and 3,6 - dimethyloctyne - (4) - diol - (3,6).

#### EXAMPLE 3

A mixture of 450 parts of 3 - methylpentyn - (1) - ol - (3) and 432 parts of methyl ethyl ketone is introduced into a suspension of 672 parts of potassium isobutyrate in 900 parts

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75

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100

105

110

115

120

125

0.8 - 1.5

1 + 1.2

82% yield

- of xylene while stirring and cooling at a temperature of about  $+5^{\circ}\text{C}$  in the course of half an hour. The mixture is then heated to  $30^{\circ}$  to  $35^{\circ}\text{C}$  and stirred for another two hours.
- 5 300 parts of water is added and a pH of from 4 to 5 is set up by adding formic acid. Distillation of the organic phase gives 720 parts of 3,6 - dimethyloctyne - (4) - diol - (3,6) having a boiling point of  $95^{\circ}$  to  $96^{\circ}\text{C}$  at 2 mm Hg.
- 10 When the same amount of potassium n-butyrate is used in this Example instead of the 672 parts of potassium isobutyrate, practically the same yield is obtained. 967.
- 15
- EXAMPLE 4
- 20 A mixture of 245 parts of 3 - methylpentyn - (1) - ol - (3) and 174 parts of acetone is reacted in a suspension of 336 parts of potassium isobutyrate and 1500 parts of xylene as described in Example 3.
- 25 325 parts of 2,5 - dimethylheptyne - (3) - diol - (2,5) is obtained; its boiling point is  $126^{\circ}$  to  $130^{\circ}\text{C}$  at 23 mm Hg.
- 30
- EXAMPLE 5
- 35 As described in Example 3, 600 parts of methyl isobutyl ketone and 630 parts of 3,5 - dimethylhexyn - (1) - ol - (3) are reacted in a suspension of 672 parts of potassium isobutyrate in 2400 parts of xylene.
- 40 950 parts of 2,4,7,9 - tetramethyldecyne - (5) - diol - (4,7) is obtained; its boiling point is  $106^{\circ}$  to  $108^{\circ}\text{C}$  at 1 mm Hg. 857.
- 45
- EXAMPLE 6
- 50 200 parts of 3 - methylbutyn - (1) - ol - (3) is introduced at a temperature of  $10^{\circ}$  to  $12^{\circ}\text{C}$  into a suspension of 336 parts of potassium isobutyrate in 1200 parts of xylene while cooling. 216 parts of isobutyraldehyde is then introduced into this mixture in the course of ninety minutes at a reaction temperature of about  $10^{\circ}\text{C}$  and reaction is allowed to continue at room temperature for another three hours.
- 55 320 parts of 2,6 - dimethylheptyne - (3) - diol - (2,5) is obtained; its boiling point is  $108^{\circ}$  to  $110^{\circ}\text{C}$  at 0.5 mm Hg.
- EXAMPLE 7
- 55 196 parts of propargyl alcohol is introduced into a suspension of 448 parts of potassium isobutyrate in 1100 parts of xylene while stirring well and cooling to  $10^{\circ}$  to  $15^{\circ}\text{C}$ . 232 parts of acetone is then introduced into this mixture in the course of two hours at  $30^{\circ}$  to  $35^{\circ}\text{C}$ .
- 55 After 300 parts of water has been added, an organic layer is separated from which 284 parts of 2 - methylpentyne - (3) - diol - (2,5) having a boiling point of  $88^{\circ}$  to  $92^{\circ}\text{C}$  at 0.5 mm Hg is obtained.
- EXAMPLE 8
- 60 As described in Example 7, 280 parts of propargyl alcohol is reacted with 540 parts of methyl ethyl ketone in a suspension of 672 parts of potassium isobutyrate in 1600 parts of xylene.
- 65 560 parts of 3 - methylhexyne - (4) - diol - (3,6) is obtained; its boiling point is  $105^{\circ}$  to  $108^{\circ}\text{C}$  at 1.5 mm Hg.
- EXAMPLE 9
- 70 112 parts of propargyl alcohol is introduced at  $10^{\circ}\text{C}$  into a suspension of 280 parts of potassium isobutyrate in 1500 parts of xylene while stirring. 150 parts of propionaldehyde is added to this mixture over two hours and the reaction temperature is kept at  $10^{\circ}\text{C}$ .
- 75 The mixture is then heated to  $25^{\circ}$  to  $30^{\circ}\text{C}$  and stirred for another three hours. 156 parts of hexyne - (2) - diol - (1,4) is obtained having a boiling point of  $110^{\circ}\text{C}$  to  $112^{\circ}\text{C}$  at 4 mm Hg.
- 80
- EXAMPLE 10
- 85 As described in Example 9, 280 parts of propargyl alcohol is first introduced at  $10^{\circ}\text{C}$  into a suspension of 672 parts of potassium isobutyrate and 1800 parts of xylene and then, also at  $10^{\circ}\text{C}$ , 432 parts of isobutyraldehyde is added over two hours.
- 90 The whole is then stirred for four hours at  $25^{\circ}$  to  $30^{\circ}\text{C}$ . 422 parts of 2 - methylhexyne - (4) - diol - (3,6) is obtained having a boiling point of  $115^{\circ}$  to  $118^{\circ}\text{C}$  at 3 mm Hg.
- EXAMPLE 11
- 95 As described in Example 9, 147 parts of 4 - methylpentyn - (1) - ol - (3) is first introduced into a suspension of 280 parts of potassium isobutyrate in 1400 parts of xylene at  $10^{\circ}\text{C}$  and then 180 parts of isobutyraldehyde is added over two hours. The mixture is heated to  $25^{\circ}$  to  $30^{\circ}\text{C}$  and stirred at this temperature for another three hours.
- 100 216 parts of 2,7 - dimethyloctyne - (4) - diol - (3,6) is obtained having a boiling point of  $128^{\circ}$  to  $131^{\circ}\text{C}$  at 15 mm Hg.
- EXAMPLE 12
- 105 210 parts of butyn - (1) - ol - (3) is introduced into a suspension of 560 parts of potassium isobutyrate and 1500 parts of xylene at  $10^{\circ}\text{C}$  and then 288 parts of n - butyraldehyde is dripped in over two hours at  $10^{\circ}\text{C}$ .
- 110 287 parts of octyne - (3) - diol - (2,5) is obtained having a boiling point of  $98^{\circ}$  to  $102^{\circ}\text{C}$  at 1.5 mm Hg.
- EXAMPLE 13
- 115 280 parts of butyn - (1) - ol - (3) is introduced at  $10^{\circ}$  to  $15^{\circ}\text{C}$  into a suspension of 560 parts of potassium isobutyrate and 1500 parts of xylene. Then 350 parts of isobutyraldehyde is added to this mixture over two hours at  $10^{\circ}\text{C}$ .

5 The whole is stirred for three hours at 25° to 30°C and then hydrolyzed with 300 parts of water and worked up. 498 parts of 2 - methylheptyne - (4) - diol - (3,6) is obtained having a boiling point of 98° to 100°C at 2 mm Hg.

EXAMPLE 14

As described in Example 13, 210 parts of butyn - (1) - ol - (3) is reacted with 400 parts of methyl isobutyl ketone in a suspension of 10 448 parts of potassium isobutylate and 1200 parts of xylene. 472 parts of 2,4 - dimethyl-octyne - (5) - diol - (4,7) is obtained having a boiling point of 93° to 95°C at 1 mm Hg.

15 EXAMPLE 15

680 parts of a 50% aqueous caustic potash solution is boiled with 3000 parts of n - butyl alcohol and over five to six hours 480 parts of an aqueous layer is separated at the top of the column from the azeotrope obtained (boiling point 92°C). While maintaining a good reflux, distillation is carried on until the temperature of the material distilling over has risen to about 117°C, which is an indication that 20 water is no longer being formed.

25 The excess butyl alcohol is distilled off without fractionation and at the end at 30 to 60 mm Hg the potassium butylate remaining in the flask is substantially freed from butyl alcohol while stirring and heating at about 150°C. The powder which remains is converted into a suspension by adding 1000 parts of benzene.

30 As described in Example 1, a mixture of 348 parts of acetone and 420 parts of 3 - methylbutyn - (1) - ol - (3) is added to this suspension. After the mixture has been stirred for another three hours at 30°C, 750 parts of water is added and the layers are separated. 35 40 621 parts of 2,5 - dimethylhexyne - (3) - diol - (2,5) is obtained from the organic layer.

EXAMPLE 16

45 A mixture of 268 parts (1 mole) of hexahydrofarnesyl acetone and 294 parts of dehydroisophytol is introduced over two hours into a suspension of 156 parts of potassium isobutylate in 1200 parts of xylene while stirring at 30° to 40°C and the reaction mixture is then stirred for about another hour. 300 parts of ice-water is added and the separated 50 organic phase is neutralized with acetic acid and freed from solvent by distillation at sub-atmospheric pressure.

55 570 parts of an oily residue is obtained which contains 7% of hexahydrofarnesyl acetone and 3% of dehydroisophytol. The remaining 90% consists of 2, 6, 10, 14, 17, 21, 25, 29 - octamethyltriacontyne - (15) - diol - (14, 17).

60 EXAMPLE 17

A mixture of 273 parts of benzophenone and 312 parts of diphenylethynylcarbinol is introduced into a suspension of 255 parts of

potassium isobutylate in 1250 parts of cumene over one hour while stirring at 35° to 40°C and the reaction mixture is stirred for another two hours. 500 parts of water is added, the organic phase is separated and neutralized and the solvent is distilled off therefrom at subatmospheric pressure. 420 parts of tetraphenylbutynediol - (1,4) having a melting point of 188° to 190°C crystallizes from the residue.

EXAMPLE 18

A mixture of 294 parts of cyclohexanone and 372 parts of ethynylcyclohexanol is introduced into a suspension of 392 parts of potassium isobutylate in 2000 parts of cyclohexane in the course of two hours while stirring at 30° to 35°C. The reaction mixture is stirred for another three hours and then 900 parts of water is added to it.

The solvent is distilled off at subatmospheric pressure from the neutral organic phase and a residue is obtained from which 465 parts of bis - (1 - hydroxycyclohexyl) - acetylene having a melting point of 108°C to 111°C is isolated by recrystallization from carbon tetrachloride.

WHAT WE CLAIM IS:—

1. A process for the production of an acetylene glycol by reacting an aldehyde or ketone with an acetylene monoalcohol in a solvent in the presence of a condensing agent - having a basic reaction, wherein the reaction is carried out in an aliphatic hydrocarbon and/or an aromatic hydrocarbon as the solvent, and a potassium alcoholate of a primary alcohol and/or of a secondary alcohol each of which has four to eight carbon atoms is used as the condensing agent.

2. A process as claimed in claim 1 wherein the condensing agent used is the potassium alcoholate of n-butanol or isobutanol.

3. A process as claimed in claim 1 or 2 wherein the reactants are used in substantially stoichiometric proportions.

4. A process as claimed in any of claims 1 to 3 wherein the condensing agent is used in a proportion of from 0.8 to 1.5 moles per mole of acetylene monoalcohol used.

5. A process as claimed in claim 4 wherein the said proportion is from 1 to 1.2 moles per mole of acetylene monoalcohol.

6. A process as claimed in any of claims 1 to 3 carried out at a temperature of from -20°C to +100°C.

7. A process as claimed in claim 6 wherein the said temperature is from 0°C to +50°C.

8. A process as claimed in any of claims 1 to 7 wherein the acetylene monoalcohol is reacted with a ketone which has the general formula (I):—



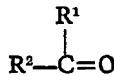
where

R<sup>1</sup> denotes a hydrocarbon or heterocyclic radical having up to twenty carbon atoms,

5 R<sup>2</sup> denotes a hydrocarbon or heterocyclic radical having up to twenty carbon atoms, or

R<sup>1</sup> and R<sup>2</sup> together with the adjacent carbon atom form a ring system which may contain nitrogen or oxygen as a hetero atom.

10 9. A process as claimed in any of claims 1 to 7 wherein the acetylene monoalcohol is reacted with an aldehyde having the general formula (I):

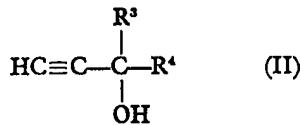


15 where

R<sup>1</sup> denotes a hydrogen atom and

R<sup>2</sup> denotes a hydrogen atom or a hydrocarbon or heterocyclic radical having up to twenty carbon atoms.

20 10. A process as claimed in any of claims 1 to 9 wherein the acetylene monoalcohol has the general formula (II);



where

R<sup>3</sup> denotes a hydrogen atom or a hydrocarbon or heterocyclic radical having up to twenty carbon atoms,

R<sup>4</sup> denotes a hydrogen atom or a hydrocarbon or heterocyclic radical having up to twenty carbon atoms, or R<sup>3</sup> and R<sup>4</sup> together with the adjacent carbon atom form a ring system which may contain nitrogen or oxygen as a hetero atom.

11. A process as claimed in any of claims 1 to 7 wherein an aldehyde or ketone named herein is reacted with an acetylene monoalcohol named herein.

12. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

13. An acetylene glycol which has been obtained by a process as claimed in any of claims 1 to 12.

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